

General procedure 9. Bis(hydroxybenzoyl)benzenes.

In a round-bottomed flask, was placed 3.6 g(9 mmoles) of a bis(methoxybenzoyl)benzene and 20 ml of 47% HBr, and the mixture was heated under reflux for more than 5 hr. The normal work-up and chromatography afforded the corresponding phenolic derivative.

General procedure 10. Bis(carboxybenzoyl)benzenes.

In a 300 ml round-bottomed flask, 1.7 g(5 mmoles) of bis-(methylbenzoyl)benzene was dissolved in a mixture of 150 ml-glacial acetic acid and 50 ml-acetic anhydride. To this solution, 6 ml of conc. H_2SO_4 followed by 20 g(0.2 mole) of chromium trioxide in three portions was added. After stirring for 1 hr at room temperature, the dark green mixture was poured rapidly onto crushed ice, followed by stirring several minutes. About 300 ml of water was added and the resulting white solid was collected by filtration followed by washing it with water.

The crystalline products were in general hardly soluble in any organic solvents, and so in some cases recrystallization was impossible. The structure could then be determined by converting it into an ester.

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Synthesis of Soluble Poly(propargyl bromide) and Poly(propargyl chloride) by Transition Metal Chlorides and Ethylaluminum Dichloride

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The polymerization of acetylene and its derivatives is one of the fundamental methods for the synthesis of polymers with a conjugated polyene system, which are beginning to be used at present time as organic semiconductors and metals.^{1,2} To date, the polymerization of propargyl bromide (PB) and propargyl chloride(PC) was attempted by the following catalysts: $PdCl_2$,³ γ -rays⁴, $Ni_2(Ph_3P)_2$,⁵ $NiBr_2(Ph_3P)_2$,⁵ $W(CO)_6-CCl_4-h\nu$,⁶ $MoCl_5$,⁷ and $MoCl_5$ -polymer⁸. However, these catalysts generally give only insoluble and intractable polymers.

Recently, we have found that transition metal chlorides and organoaluminum compounds are very effective for the polymerization of some acetylene derivatives such as 1-chloro-2-thienylacetylene,⁹ 2-ethynylpyridine,¹⁰ and dipropargyl derivatives.¹¹⁻¹³

The present communication reports that PB and PC could be effectively polymerized by the binary catalyst systems composed by transition metal chlorides (WCl_6 , $MoCl_5$, and $TiCl_4$) and $EtAlCl_2$ to give polymers in high conversions. In

some cases the polymers obtained were soluble in solvents and high molecular weight materials.

All the preparative procedures of catalysts and polymerization were carried out under dry nitrogen atmosphere.

As shown in Table 1, WCl_6 alone gave only moderate yield of polymers. However, $TiCl_4$ failed to give any polymeric product. $EtAlCl_2$ was found to be very effective co-catalyst in the polymerization of PB and PC when used with transition metal chlorides. The ratios of the portion of soluble polymeric product to insoluble product portion varied depending on the catalyst system used. $TiCl_4-EtAlCl_2$ gave completely soluble polymer, even though the polymer yield was low. The number-average molecular weight(\bar{M}_n)s of the resulting soluble polymers were in the range of 8,700 to 19,500.

The ^{13}C -NMR spectrum of poly(propargyl bromide) (PPB) showed the presence of the olefinic carbons at about 129 and 135 ppm and the methylene carbon at 40 ppm. In the UV-visible spectra of PPB and poly(propargyl chloride)

Table 1. Polymerization of Propargyl Bromide and Propargyl Chloride by Transition Metal Catalysts^a

Experiment number	Monomer	Catalyst System ^b (mole ratio)	Polymer			\bar{M}_n^d
			Yield(%) ^c			
			Sol. ^e	Insol.	Total	
1	PB	WCl ₆	10	20	30	8,700
2	PB	WCl ₆ -EtAlCl ₂ (1:4)	46	32	78	18,200
3	PC	WCl ₆	11	29	40	9,400
4	PC	WCl ₆ -EtAlCl ₂ (1:4)	61	30	91	19,500
5	PC	MoCl ₅ -EtAlCl ₂ (1:4)	64	11	75	17,600
6 ^f	PB	TiCl ₄ -EtAlCl ₂ (1:4)	52	0	52	10,100
7 ^f	PC	TiCl ₄ -EtAlCl ₂ (1:4)	42	0	42	9,700

^aPolymerization was carried out in chlorobenzene for 24 hrs. at 40°C. Monomer to catalyst mole ratio(M/C) was 50. Initial monomer concentration([M]₀) of PB and PC were 1 and 1.5M, respectively. ^bMixture of catalyst and cocatalyst was aged at 30°C for 15 min. before use. ^cMethanol-insoluble polymer. ^dDetermined by GPC in tetrahydrofuran using a calibration curve for polystyrene. ^eSoluble polymer in chloroform. ^fPolymerization solvent was benzene.

(PPC), a characteristic peak of the conjugated double bond, broad and weak $\pi \rightarrow \pi^*$ absorption, appeared at visible region(400-580 nm). The IR spectra of PPB and PPC showed an absorption at 1600cm⁻¹ owing to the stretching frequency of conjugated double bond in the polymer backbone. From these spectral data, it was concluded that these polymers possess conjugated polyene structures.

More detailed study on the polymerization of the acetylene monomers by other transition metal catalysts and the physical properties of the resulting polymers are in pro-

gress.

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Micellar and Metal Ion Effects on the Reactions of 1,4-Dihydronicotinamide

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1,4-Dihydronicotinamides are widely investigated, mainly as model compounds of the coenzyme NADH.¹ While NADH and its model compounds can reduce various functionalities, they are known to be unstable in aqueous medium and undergo acid catalyzed hydration reaction.² Thus most NADH mimic reductions of organic substrates have been performed in non-aqueous media. For efficient NADH reductions in biological systems which is obviously aqueous, there must be some mechanisms which retard the hydration reaction and accelerate the reduction reactions. This can be achieved by the interactions of the coenzyme with the NADH-dependent enzymes and substrates. The catalysis of metal ions is necessary for reduction reactions in alcohol dehydrogenases that require NADH as a cofactor.³ Similarly, it was found that the metal ions have large effects on NADH

mimic reductions in non-aqueous media.¹ The surfactant micelles are extensively utilized as enzyme mimetic systems.⁴ It was reported that the micelles greatly affect the hydration reaction of NADH model compounds.⁵ The reactions of NADH model compounds in surfactant micellar solutions containing metal ions would mimic the reactions in biological systems more closely. In this communication, we wish to report the micellar and metal ion effects on the reduction of 2,2,2-trifluoroacetophenone (TFA) by 1-benzyl-1,4-dihydronicotinamide (BNAH) and the hydration of BNAH.

1-Benzyl-1,4-dihydronicotinamide was prepared by reaction of 1-benzyl-3-carbamoylpyridinium salt by sodium dithionite.⁶ Kinetic studies were performed in 0.01 M surfactant (CTAB or SDS) medium containing 2% 2-propanol of pH 7.0. 0.01 M cacodylate was used for pH 7.0 buffer solu-